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# SEQUENTIAL (ANAEROBIC/AEROBIC) BIOLOGICAL TREATMENT OF DALAMAN SEKA PULP & PAPER INDUSTRY EFFLUENT

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# PULP & PAPER INDUSTRY

- is one of the most significant industries in many countries' economies
  - 5th largest industry in North America's economy *(Nemerow and Dasgupta, 1991)*
  - In Canada, the pulp and paper industry accounts for a major portion of the country's economy in terms of value of production and total wages paid *(Sinclair, 1990).*

# PULP & PAPER INDUSTRY

- The world production of paper and board is about 320 million tons/year – 1996 data

  *(Doble and Kumar, 2005)*

  - North America produces more than 50%
  - Western Europe produces ~ 20%
  - Japan produces ~ 12%

# PULP & PAPER INDUSTRY

The world production of paper and board in the continents (1998 data)

| The Continents | Capacity | | Production | |
|---|---|---|---|---|
| | % | Ton (*$10^6$) | % | Ton (*$10^6$) |
| America | 37.46 | 130.936 | 39.35 | 118.445 |
| Europe | 29.70 | 103.838 | 29.98 | 90.247 |
| Asia | 30.72 | 107.384 | 28.55 | 85.947 |
| Australia | 1.05 | 3.650 | 1.12 | 3.377 |
| Africa | 1.07 | 3.733 | 1.00 | 2.996 |
| **TOTAL** | 100.0 | **349.541** | 100.0 | **301.012** |

*(Pulp and Paper Industry Foundation Report, 1998)*

# PULP & PAPER INDUSTRY in TURKEY

- The first pulp & paper industry was established in Izmit in 1934, with a capacity of 12,000 ton/year.
- By 2000, the total capacity of this industrial sector has increased to 1,822,000 ton/year (both public and private sector).
  - 7 pulp and paper industries (public sector, yet to be privatized)
  - 31 private pulp and paper industries
- The pulp and paper production of Turkey was 1,356,000 ton/year in 1998.

*(State Planning Organization Commission Report, 2000)*

# PULP & PAPER INDUSTRY in TURKEY

- Pulp and paper production capacity of Turkey has increased by **43%** within the years 1992-1998.
- Yet, its capacity is 2% of the EU's capacity.
- Consumption of paper-cardboard;
  - 31.7 kg/capita in Turkey
  - 190.3 kg/capita in EU (average)
- In Turkey, 38.8% of the consumption is being imported.

(*State Planning Organization Commission Report, 2000)*

# PULP & PAPER INDUSTRY in TURKEY

- Pulp and paper industry is still developing in Turkey,
  - Modernization of the equipments is needed for some of the industries
- To be able to compete, the cost of the production is to be decreased.
- The main reasons of costly production;
  - Low quality resources (wood, etc.)
  - High electricity charge (0.077 $/KWh)
  - Low quality and inadequate amount of secondary resources (kaolin, etc.)
  - Recovery and reuse technology to be widespread applied
  - The percentage of the waste paper recovery (34.5%) to be increased.

*(State Planning Organization Commission Report, 2000)*

# PULP & PAPER INDUSTRY

- **High water usage;**
  - ranks third in the world, after the primary metals and chemical industries, in terms of freshwater withdrawal *(Thomson et al., 2001).*
  - 20000 – 60000 gallons per ton of product

    *(Nemerow and Dasgupta, 1991)*
  - Consumption of water varies depending on the type of paper being produced;
    - Manufacture of tissue: 60 $m^3$/ton
    - Manufacture of printing and writing paper: 35 $m^3$/ton
    - Manufacture of newsprint : 30 $m^3$/ton
    - Manufacture of packaging material: 18 $m^3$/ton

      *(Doble and Kumar, 2005)*

# PULP & PAPER INDUSTRY

Accordingly,

- Pulping process produces a considerable amount of wastewater, about 200 $m^3$/ton of pulp produced

  *(Doble and Kumar, 2005)*

  - Fiberboard manufacturing; 3-15 $m^3$/ton of board
  - As low as 1.5 $m^3$/ton of paper produced, or, 60 $m^3$/ton of paper produced

    *(Thomson et al., 2001; Asghar et al., 2008)*

  - 75-225 $m^3$/ton of paper produced in Indian pulp & paper industry *(Tewari et al., 2004)*

# PULP & PAPER INDUSTRY

***The cost of the treatment is high in relation to the cost of the product produced. Thus economic limitations have forced the industry to place emphasis on recovery rather than treatment..***

*The concept of "zero liquid effluent" has been suggested for mills making certain grades of paper or when water sources are extremely limited..* ***Yet, for majority of the industries, wastewater remains to be treated..***

# MAIN PROCESSES in a PULP & PAPER INDUSTRY

- The main processes that are involved in the manufacture of paper are
  - debarking,
  - pulping,
  - separation of pulp from cooking liquor,
  - bleaching,
  - stock preparation
  - making the final paper product.

# PULP & PAPER INDUSTRY EFFLUENT

## GENERAL CHARACTERISTICS

- high lignin content,
- high absorbable organic halide (AOX) concentration (due to bleaching process),
- phenolic compounds, VOCs
- color,
- low biodegradability (high chemical oxygen demand to biochemical oxygen demand ratios; COD/BOD= 4–6),
- potential toxicity problems.

# PULP & PAPER INDUSTRY EFFLUENT

- In the bleaching process, lignin and other color compounds are removed by chemical agents. The oxidation agents used for bleaching, central to the industry, are chlorine-based such as $Cl_2$, $ClO_2$, hypochlorite, NaOCl, etc.

- There are also oxygen-based oxidation agents (such as $H_2O_2$, $O_3$, etc.)..

# PULP & PAPER INDUSTRY EFFLUENT

- Use of chlorine-based agents results in the production of degradation products which include various chloro-organic derivatives.

***Treatment of bleaching process wastewater externally is necessary;***

***Treatment of pulp and paper industry effluents containing chlorinated compounds is still of vital importance.***

# PULP & PAPER INDUSTRY EFFLUENT

## TREATMENT TECHNOLOGIES

- **Primary treatment**
- **Secondary treatment**
  - Physicochemical treatment
    - sedimentation, coagulation, flotation, screening, adsorption, oxidation, electrolysis, RO, UF, NF
  - Biological treatment
    - lagoons,
    - activated sludge,
    - anaerobic treatment.

# TREATMENT OF PULP & PAPER INDUSTRY EFFLUENT

- **By chemical precipitation, removal efficiencies of**
  - 20–85% for AOX,
  - 20–90% for COD
  - 36–100% for color

  *…depending on the coagulant and studied wastewater*

- **By oxidation,** 100% color removal

- **By ozonation (combined with UV or photocat.)**
  - 50-90% for AOX
  - 57-85% for COD
  - 60-100% for color

# TREATMENT OF PULP & PAPER INDUSTRY EFFLUENT

- **By aerobic biological treatment - by lagoons and activated sludge systems-, removal efficiencies of;**
  - 65-99% BOD
  - 25-65% COD
  - 40-50% AOX
- **By anaerobic treatment; removal efficiencies of;**
  - 70-97 % BOD
  - 40-85% COD

# TREATMENT OF PULP & PAPER INDUSTRY EFFLUENT

- **By anaerobic biological treatment;**
  - COD removal of 66%, were obtained using a UASB reactor with an HRT of 6 h *(Chen and Horan, 1998)*
  - COD removal efficiency of 80% was constantly achievable but the residual COD (around 800 mg/l) means additional treatment was essential.

    (Thompson et al., 2001)

# TREATMENT OF PULP & PAPER INDUSTRY EFFLUENT- TURKEY

- **Among 24 pulp and paper industries, constituting the 90% of the production in the country;**
  - 21 industries have treatment systems;
    - 7 of them have physiochemical treatment
    - 13 of them uses physiochemical + biological treatment
    - 2 of them have biological treatment..

***As biological treatment; activated sludge, anaerobic systems, or, aerated lagoons are employed..***

*(State Planning Organization Commission Report, 2000)*

# OBJECTIVE OF THE STUDY

- Pulp and paper industry effluent from Dalaman SEKA Pulp and Paper Industry was examined for its **toxic effects on anaerobic microorganisms** by anaerobic toxicity assay.

- Additionally, this wastewater was applied to a **sequential biotreatment** process consisting of
  - an UASB as the anaerobic stage and
  - a once-through CMSTR as the aerobic stage.

# DALAMAN SEKA PULP & PAPER INDUSTRY


***Established in:*** ***1971***

***Privatization in:*** ***2001- MOPAK***

***Product type:*** *paper and cardboard production, kraft cellulose*

# DALAMAN SEKA PULP & PAPER INDUSTRY

***Established in:*** ***1971***

***Privatization in:*** ***2001***

***Product type:*** *paper and cardboard production, kraft cellulose*

***Capacity:*** *75,000 ton/year – kraft cellulose*

***Capacity:*** *123,000 ton/year– paper and cardboard*

***Production:*** *66,647 ton/year- kraft cellulose;*

*86,667 ton/year - paper and cardboard;*

*(year, 2003)*

# WASTEWATER CHARACTERISTICS

Pulp and paper effluent (PPE) was obtained from Dalaman SEKA Paper Industry, Turkey. During the entire research, PPE was taken twice from the industry (PPE-1, PPE-2).

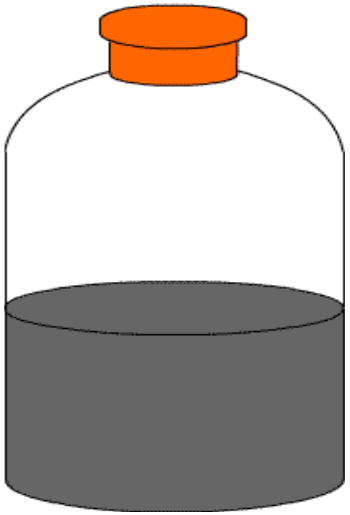
**PPE-1;** COD: 450–500 mg/l, VSS: 51 ±4 mg/l,

**PPE-2;** COD: 5500–6000 mg/l, VSS: 820 ±28 mg/l

# EXPERIMENTAL STUDY - 1

- **BATCH REACTOR EXPERIMENTS**

to investigate the toxicity of pulp & paper effluent (PPE-1) on anaerobic sludge, an anaerobic toxicity assay (ATA) experiment was conducted



**125 mL batch reactors**

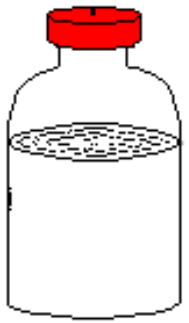
**SEED SLUDGE:** Anaerobic digesters of the Ankara Municipal Wastewater Treatment Plant

HRT = 14 days
pH = 7.00 - 7.70.

# BATCH REACTOR EXPERIMENTS

*PROCEDURE:*

1. Addition of seed sludge (VSS= 15000 ± 35 mg/l)
2. Addition of basal medium
3. Flushing with $N_2/CO_2$ (75/25) gas mixture for 3-4 min.
4. Incubating the bottles in the hot room at $35\pm2^0C$.



Basal medium content

| | Concentration (mg/L) |
|---|---|
| $NH_4Cl$ | 1200 |
| $MgSO_4.7H_2O$ | 400 |
| KCl | 400 |
| $Na_2S.9H_2O$ | 300 |
| $CaCl_2.2H_2O$ | 50 |
| $(NH_4)_2HPO_4$ | 80 |
| $FeCl_2.4H_20$ | 40 |
| $CoCl_2.6H_20$ | 10 |
| KI | 10 |
| $MnCl_2.4H_20$ | 0.5 |
| $CuCl_2.2H_20$ | 0.5 |
| $ZnCl_2$ | 0.5 |
| $AlCl_3.6H_20$ | 0.5 |
| $NaMoO_4.2H_2O$ | 0.5 |
| $H_3BO_3$ | 0.5 |
| $NiCl_2.6H_20$ | 0.5 |
| $NaWO_4.2H_2O$ | 0.5 |
| $Na_2SeO_3$ | 0.5 |
| Cysteine | 10 |
| $NaHCO_3$ | 6000 |

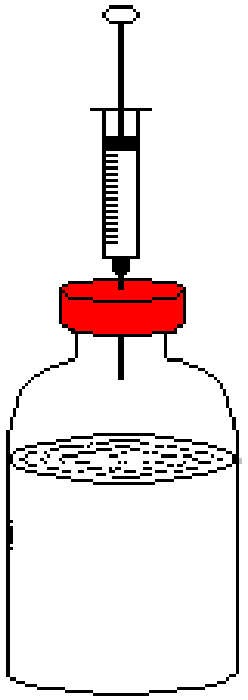
# BATCH REACTOR EXPERIMENTS

*PROCEDURE:*

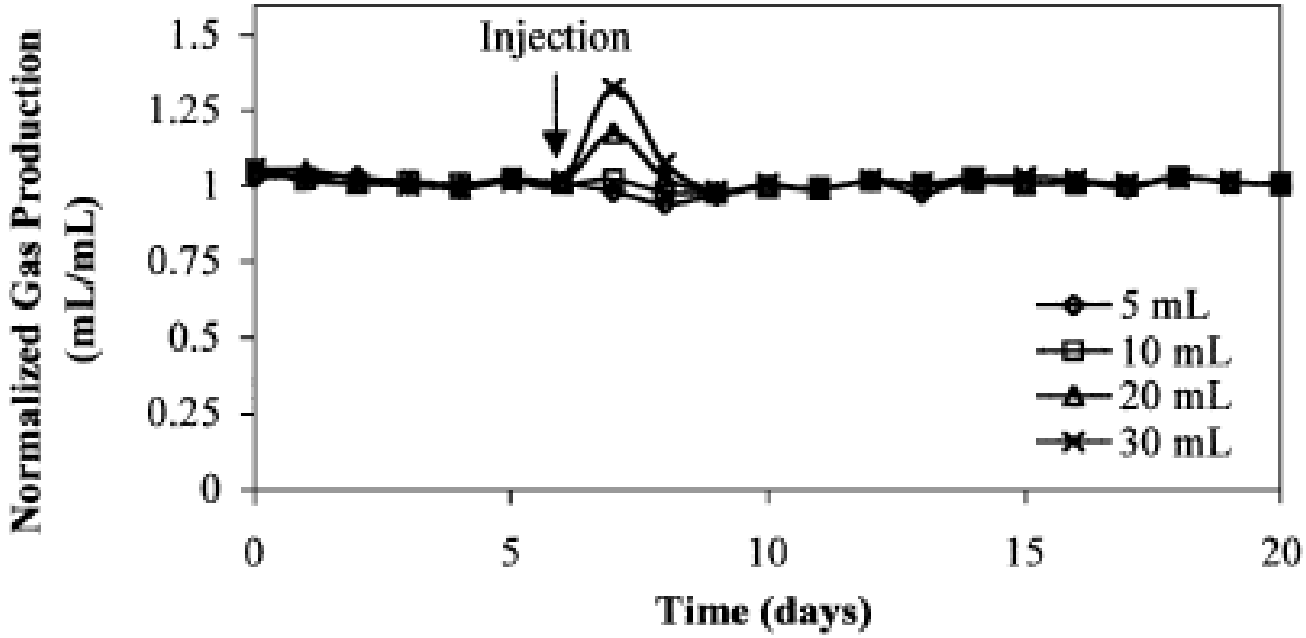
5. Daily **acetic acid** addition, to stochiometrically restore HAc concentration to 1050 mg/l daily, depending on the gas produced the previous day.

6. After observing steady state gas production (i.e. the daily variation in gas production <10%), **5, 10, 20, 30 mL of PPE** were injected into the bottles.

7. After spiking, the monitoring of the gas production for the following 14 days.



# BATCH REACTOR EXPERIMENTS




*RESULT:*

*PPE-1 had no inhibitory effect on anaerobic microorganisms under studied conditions*

# EXPERIMENTAL STUDY - 2

- **CONTINUOUS REACTOR EXPERIMENTS**

to investigate the anaerobic treatability and sequential anaerobic/aerobic treatability of the pulp & paper effluent..

***First part of the study:***

*Upflow anaerobic sludge blanket (UASB) reactor*

***Second part of the study;***

*UASB reactor + Completely mixed stirred tank reactor (CMSTR)*

# CONTINUOUS REACTOR EXPERIMENTS

## ***UASB REACTOR***

Cylindrical columns; Inner D: 5.2 cm, Length: 1 m

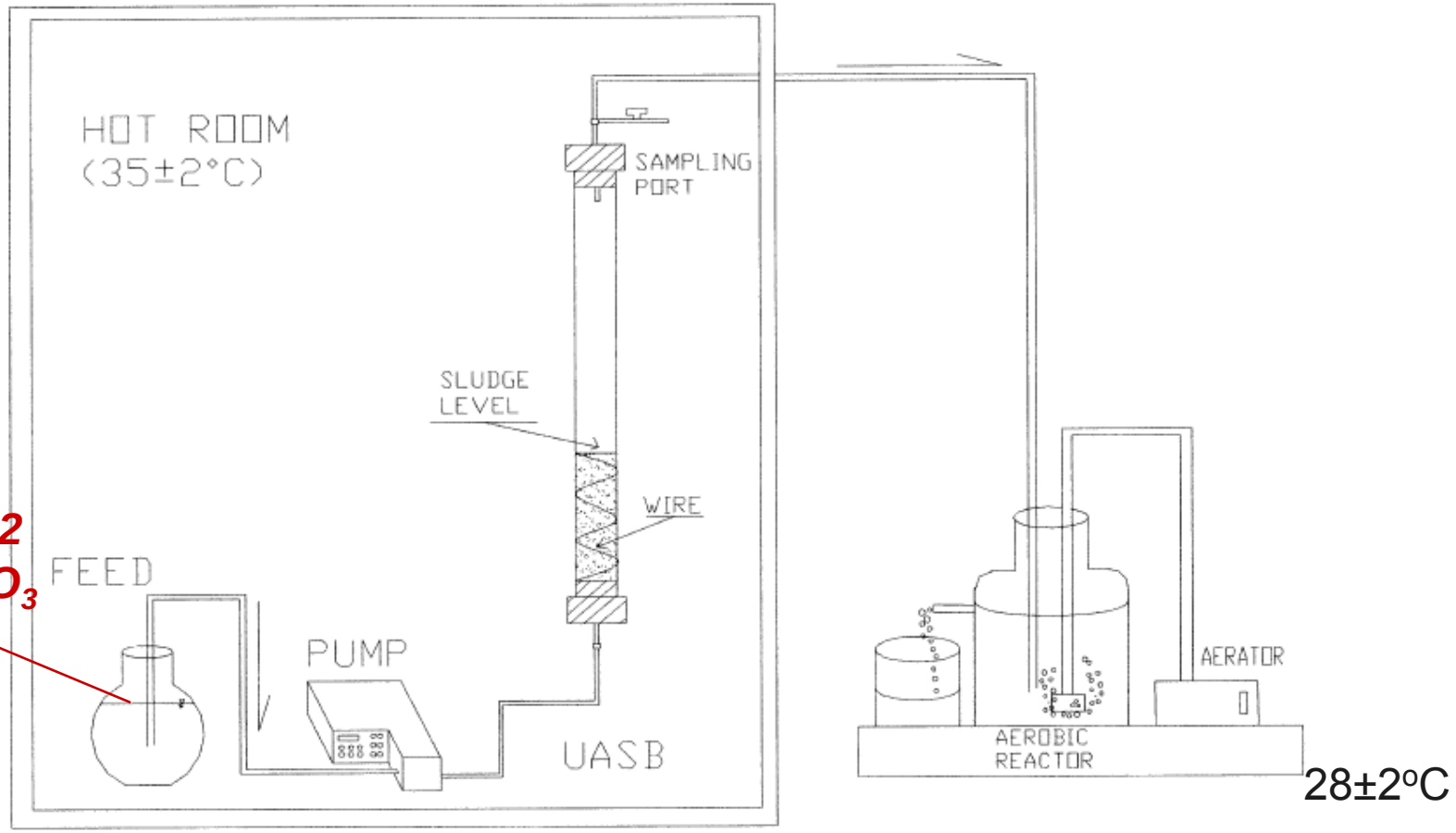
*Anaerobic granules: from the wastewater treatment plant of Tekel Pasabahce Factory, Istanbul, Turkey.*
(OLR = 30 kg COD/$m^3$.day, pH = 6.0–9.0)

## ***CMST REACTOR***

1-L of reactor volume, without any recycle

*Aerobic cultures:* from the aeration tanks of the activated sludge units of the Ankara Municipal Wastewater Treatment Plant.
(SRT: 2.8 days, OLR: 165,000 kg $BOD_5$/day)

# CONTINUOUS REACTOR EXPERIMENTS




***Pulp & paper industry effluent + 2 g/L $NaHCO_3$***

**Schematic illustration of the sequential reactor system**

# CONTINUOUS REACTOR EXPERIMENTS

- **Both PPE-1 and PPE-2 were fed to the reactors,**

PPE-1 for the first 35 days

only UASB reactor was on operation..

PPE-2, for the following days;

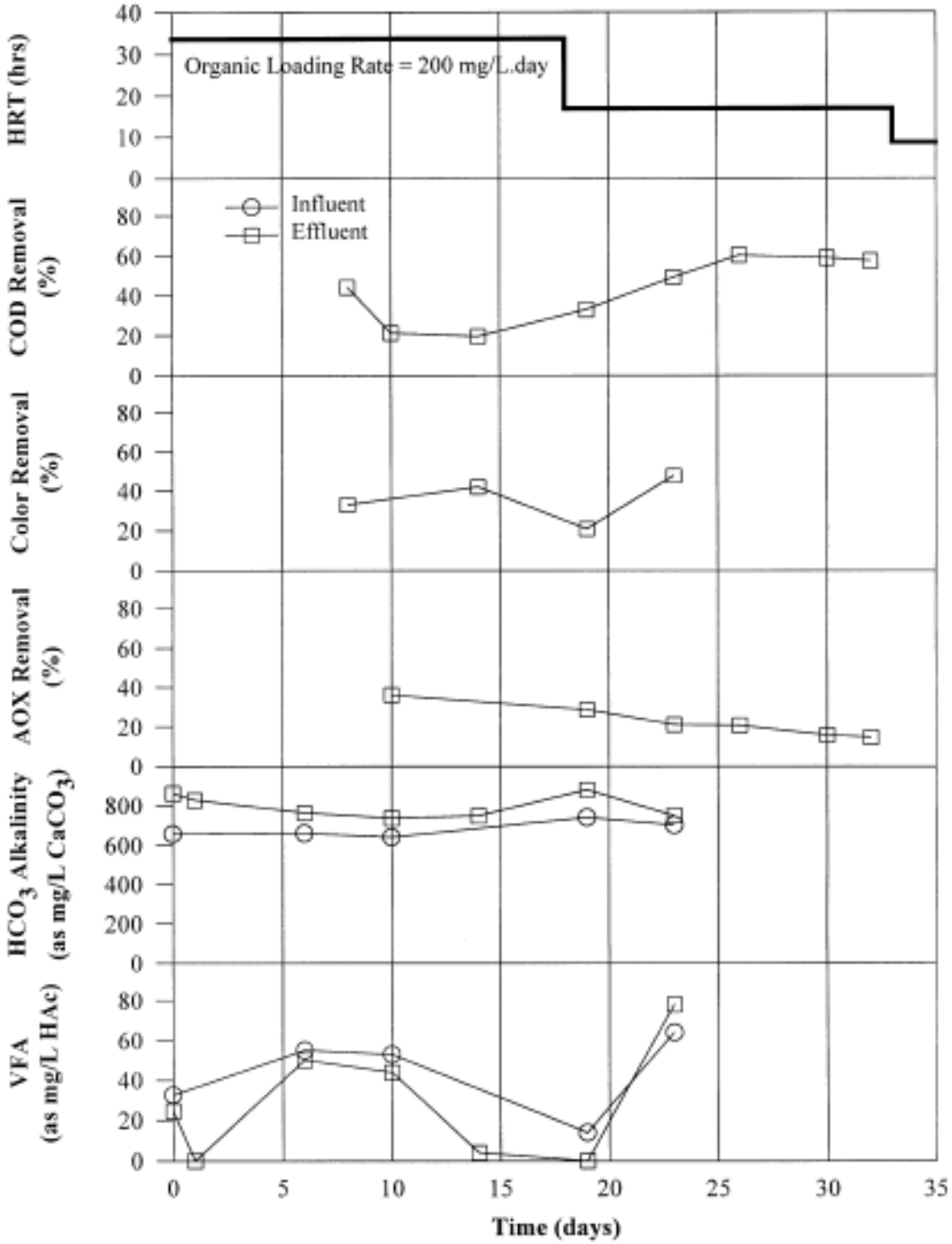
CMSTR was involved in addition to UASB Reactor

i.e., sequential anaerobic + aerobic system

***PPE-1;*** *COD: 450–500 mg/l, VSS: 51 ±4 mg/l,*

***PPE-2;*** *COD: 5500–6000 mg/l, VSS: 820 ±28 mg/l*

- PPE-1



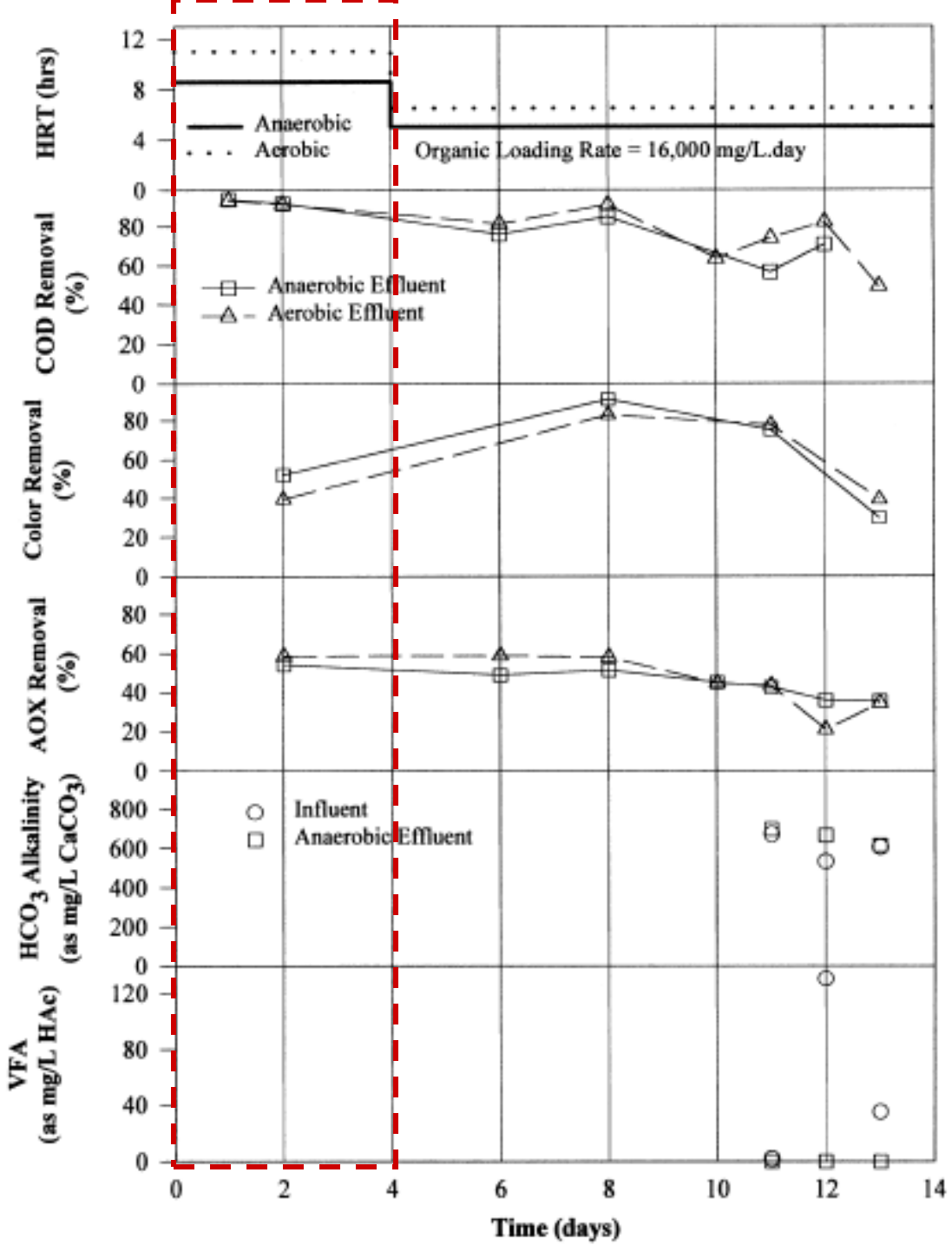

***Max. COD removal: 60%***

***Max. color removal: 46%***

***Max. AOX removal: 45%***

***(HRT:34 h)***

- **PPE-2**




***UASBR***

***HRT: 8.6 h***

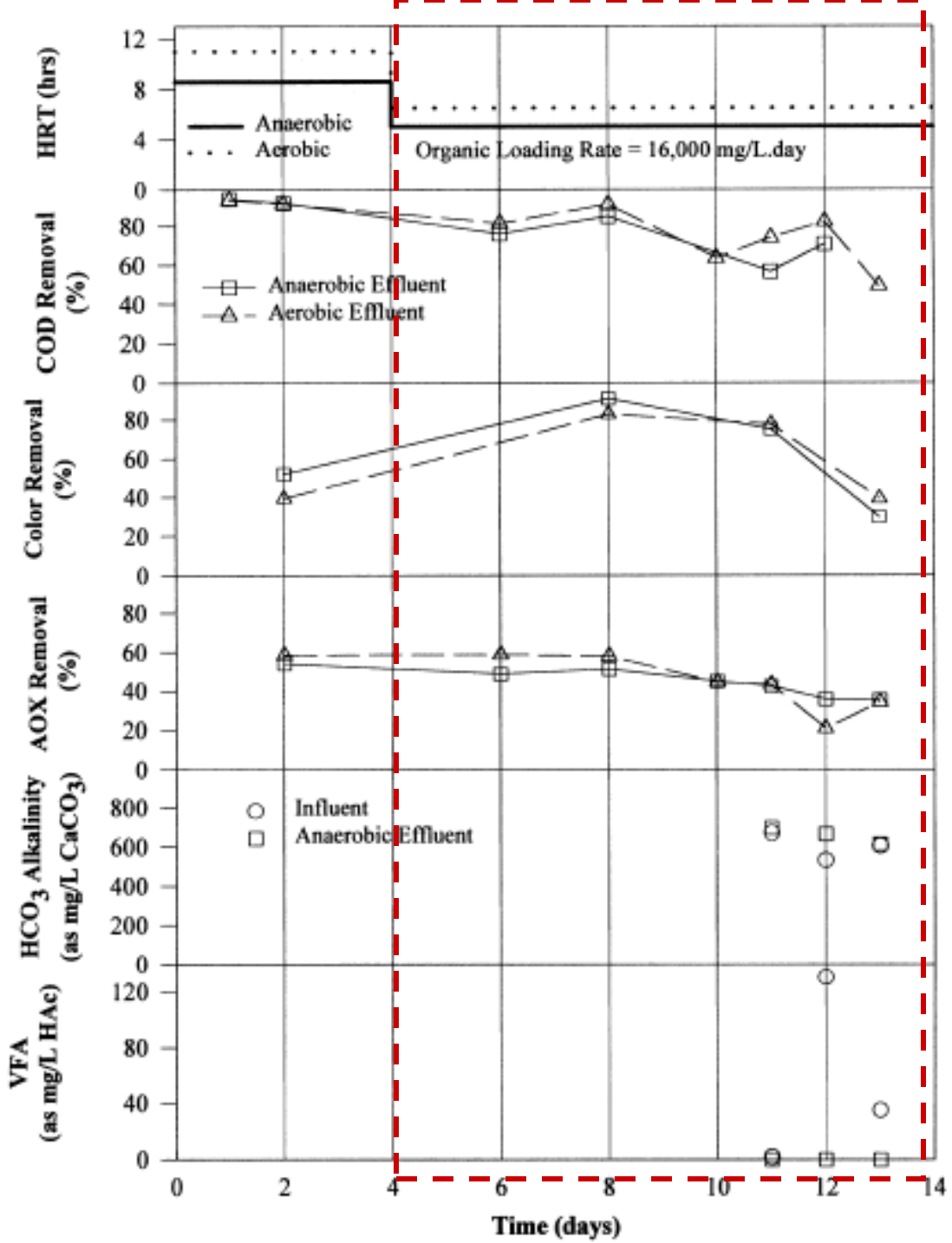
***Max. COD removal: 96%***

***Max. color removal: 52%***

***Max. AOX removal: 52%***

***No additional COD removal with aerobic stage, yet, additional 5% color removal..***

- **PPE-2**




***UASBR***

***HRT: 5 h***

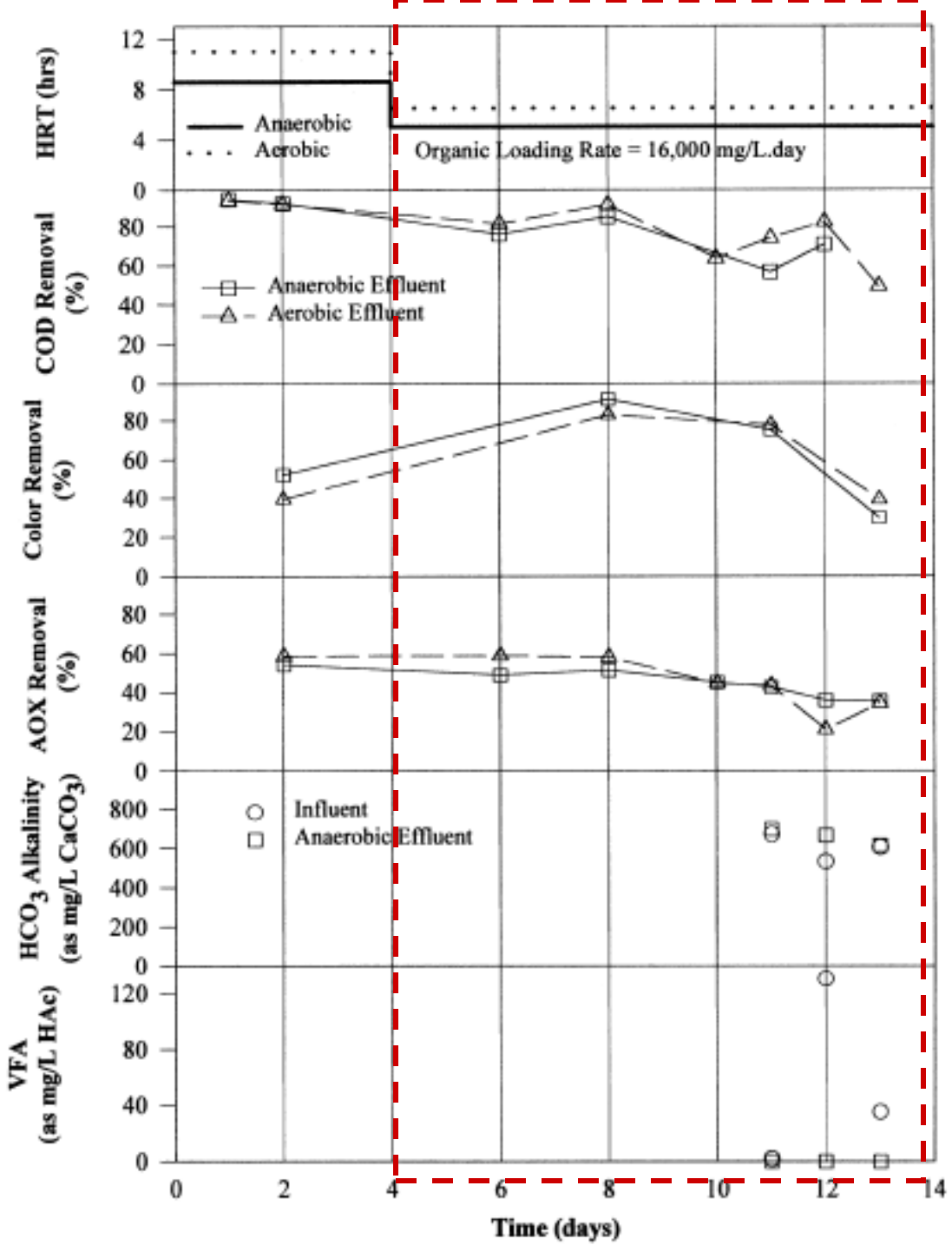
***Max. COD removal: 85%***

***Max. color removal: 90%***

***Max. AOX removal: 50%***

***With aerobic stage, additional, 8% AOX and 6% COD removal..***

- **PPE-2**




***UASBR***

***HRT: 5 h;***

***CMSRT:***

***HRT: 6.5 h;***

***Total COD removal: 91%***

***Max. AOX removal: 58%***

# CONCLUSIONS

- Dalaman SEKA Pulp and Paper Industry wastewater exerted no inhibitory effects on the anaerobic cultures under the studied conditions
- Application of a sequential biological (anaerobic/ aerobic) system resulted in approximately 91% COD and 58% AOX removals at an HRT of 5.0 and 6.5 h for anaerobic and aerobic systems, respectively.
- AOX removal efficiency is promising when compared with the separate application of conventional aerobic and anaerobic treatment.
- Color removal efficiency of 90% was achieved in the anaerobic reactor at an HRT of 5.0 h. Addition of an aerobic reactor to the system did not affect the color removal significantly.

# CONCLUSIONS

- When the **economic concerns and the rate of treatment** are considered, anaerobic treatment can offer a viable treatment option for these wastewaters.
- Cost/benefit analysis should be applied..
- Waste minimization, good-house keeping, internal process changes will minimize the amount of wastewater produced..
  - For reuse practices, tertiary treatment might be required.

# THANK YOU FOR LISTENING

# TREATMENT OF PULP & PAPER INDUSTRY EFFLUENT

- **By combined chemical and biological treatment,**
  - AOX reduction: 53 - 59% *(Francis et al., 1997)*

    … depending on the operating conditions of the biological treatment process.

  - pre-ozonation + activated sludge;
    - increased BOD removal (from 22-60% to 91%), increased COD removal (from 47-62 to 85%)

      *(Tuhkanen et al., 1997)*